

# ENAMELS

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## ENAMELING OF BRASS

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The reasons for the origination of defects in enameling watch bracelets made of L-90 brass are investigated using the methods of chemical and microstructural analysis. It is demonstrated that the defects are due to the increased content of bismuth and lead in the alloy. A method for eliminating the defects is proposed.

Copper and copper alloys are frequently used in producing jewelry and ornaments, badges, and accessories. These alloys are usually double brass (for instance, L-90) mostly used as deformable alloys. L-90 brass (tombac, 10% Zn) has good mechanical and corrosion properties, is excellent for pressure treatment in hot and cold state, has an attractive golden color, and is suitable for cladding, gilding, and enameling.

Enameling is carried out using lead and lead-free clear and opacified borosilicate enamels. The enamels have to meet a number of requirements: be resistant to mineral acids, low-melting, moisten well the surface of enameled metal, and have an attractive appearance. All these requirements are satisfied by the enamels developed at the Institute of General and Inorganic Chemistry of the National Academy of Sciences of Belarus (RF patent No. 2081071; Belarus patents Nos. 1107 and 2422). The specified enamels have good adhesion to brass L-90, equal to 50 kg/cm<sup>2</sup>.

The formation of enamel coatings is based on reactions of the metal surface with enamel at the phase boundary. The coating quality is determined by the properties of the enamel, primarily, its wettability depending on viscosity and surface tension, as well as the structure and relief of the surface, the composition, and the structure of the surface films on the metal. Therefore, metal articles are brought to an equilibrium state before enameling, and their surface is subjected to special treatment. This treatment includes purification and degreasing of the surface by pickling and shot-blasting, development of oxide or other (nickel, phosphate) films through chemical or thermal treatment, etc. A further modification of the state of the surface takes place in the course of the interaction between enamel and metal, which has an effect on the strength of adhesion of enamel to metal.

One of the most significant factors controlling the enameling process is the structure of the metal depending on preliminary treatment and on the composition.

As the limiting solubility of zinc in copper at room temperature is 38 – 39% and virtually does not change until the temperature of 453°C, brass L-90 (according to the phase diagram) has the structure of the  $\alpha$ -phase. The phase composition of brass is not modified in hot pressing and decorating. Thus, brass with a zinc content above 12% is not enameled. There are data indicating that the size of the metal grains and the phase morphology in multiphase alloys significantly affect the enameling process.

The purpose of the present study was to investigate the reasons for the emergence of defects in enameling the “crab”-shaped watch bracelets produced at the Minsk Watch Works and to identify methods for eliminating these defects. The defects include flaking and splitting-off of the enamel layer from the edges of the metal substrate [1, 2], and such defects can originate even when using the same batch of enamel and when the brass composition meets the standard state requirements.

To identify the reasons for weak adhesion of enamel to brass and for the origin of defects, the chemical analysis of the metal was carried out and the obtained results are listed in Table 1.

The defective samples exhibit a substantial excess of bismuth and lead content over the maximum permissible content for deformable copper alloys. Thus, the lead content exceeds the prescribed values by 10 – 16 times, and the bismuth content is 1.5 – 2.5 times higher than the prescribed norm. The iron content in a defective sample is 10 times higher than in a sample without defects.

The impurities forming low-melting eutectics and brittle chemical compounds with copper deteriorate the mechanical properties of brass and significantly lower its capacity for deformation [3]. The most common impurities in brass are iron,

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TABLE 1

Sample	Weight content in metal, * %			
	Fe	Pb	Bi	Zn
Without defect	0.0420	0.0052	–	9.5000
Defective	0.3300 – 0.5300	0.0500 – 0.0800	0.0030 – 0.0058	10.0000 – 12.0000
Maximum permissible component	0.10 – 0.20	0.003	0.002	12.000

\* Remainder Cu.

bismuth, lead, antimony, arsenic, and phosphor. Iron in small quantities has no perceptible effect on mechanical properties of brass [4]. Lead and bismuth have a negative effect on mechanical and technological properties of double brass. They form eutectics with copper, which consist nearly of pure metal (the bismuth content in such a eutectic is 99.8%, that of lead is 99.94%). Due to the nearly total insolubility of lead and bismuth in solid copper, these eutectics, regardless of their content, emerge in alloys, are the last to crystallize, and are located along the boundaries of the copper grains. A eutectic rich in bismuth produces the finest interlayer between the copper grains and the thickness of this interlayer according to some data can reach several atomic layers. Therefore, the presence of thousandths of a percent of bismuth is usually sufficient to form such interlayer on a substantial part of the intergrain surface.

Lead, similarly to bismuth, forms a fine low-melting interlayer along the copper grain boundaries, which is visible in the form of a grid on a polished section.

Bismuth and lead impurities even in the smallest quantities (from tenths to thousandths of a percent) significantly decrease the plasticity of copper at elevated temperatures. Bismuth due to its brittleness decreases the plasticity of copper in the cold state.

The negative effect of such impurities to a large extent can be neutralized by introducing additives that bind the impurities into chemical compounds. This facilitates a substantial purification of the grain boundaries, and a significant part of the inclusions becomes located inside the copper grains. However, such a variant of treatment is impossible in this case, since brass is supplied as a rolled product. A solution for this problem had to be found in thermal treatment of the intermediate product.

A comparative analysis of brass samples was carried out using a Neophot-21 microscope. Figure 1 shows the microstructure of the surface of the metal samples at the spot where enamel is applied. The sample that exhibited defects in enameling (having an elevated content of lead and bismuth impurities) has fine grains of size 40 – 60  $\mu\text{m}$ . The grain size in the sample whose chemical composition meets the standard requirements is 80 – 160  $\mu\text{m}$ . The above difference is related to the modifying effect of excessive bismuth and lead. These elements are surfactant modifiers with respect to copper and ensure a significantly fine grain size

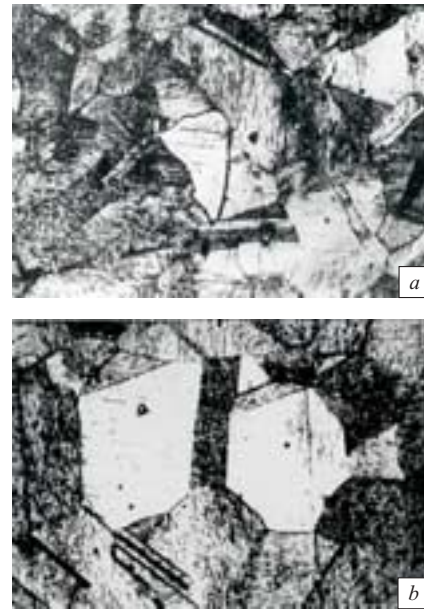


Fig. 1. Microstructure of L-90 brass: a) sample exhibiting defects in enameling; b) sample without defects.

when present in an amount ranging from 0.001 to 0.100%. The increased extent of the intergranular boundaries presumably decreases the adhesion of enamel to tombac.

The differences in microstructure do not influence the microhardness of metal. The microhardness of both samples is 1330 MPa, and the Rockwell hardness is 68 HRB. The incoming quality control at the factories is carried out by measuring the microhardness and Rockwell hardness; however, such control cannot identify the suitability of metal for enameling. Apparently, measuring hardness cannot be regarded as a reliable control method, especially measuring microhardness, which is determined inside local volumes, usually inside the grain.

It is possible to neutralize the existence of toxic impurities in an intermediate watch bracelet by selecting a special annealing regime directed to enlarging the grains.

To eliminate the defects, recrystallization annealing was carried out to ensure the enlargement of the grain. According to the Bochvar formula [5, 6], the recrystallization temperature is determined by the relationship

$$T_r = aT_m,$$

where  $T_r$  and  $T_m$  are the absolute temperatures of recrystallization and melting;  $a$  is the coefficient depending on the purity of metal.

The coefficient  $a$  for alloys can reach 0.8. The melting point of L-90 brass is 1025°C, the temperature of recrystallization annealing is 770°C.

As a result of annealing, the size of the brass grain was 100 – 120  $\mu\text{m}$ . The enameling of the samples after their recrystallization annealing demonstrated that the defects are absent from their enameled surface.

The suitability of metal for enameling should be established based on the results of a quantitative microstructural analysis. The optimum structure of copper and copper alloys for enameling has a grain size of 80 – 180  $\mu\text{m}$ .

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